

Final Project Report for ER15351
“A Study of New Actinide Zintl Ion Materials”

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I. Introduction

During the project, annual reports have been submitted that described the work accomplished. This report will summarize those reports. During the grant period, one Ph.D. student finished his degree and transitioned to a postdoc position and was hired as a staff member at Los Alamos National Laboratory (Dr. Ryan F. Hess). Three postdocs were hired: Dr. Paula Briggs-Piccoli (University of Arizona), Dr. Benny C. Chan (Penn State University) and Dr. Hugh D. Selby (University of Arizona). Dr. Briggs-Piccoli was hired on as a staff member at Argonne National Laboratory, Dr. Chan has been teaching at The College of New Jersey, and Dr. Selby was hired on as a staff scientist at Los Alamos. Four undergraduate students at Colorado State were also trained during the project period and appear as coauthors on our papers: Ms. Sarah Wilhelms (staff scientist in Boulder, CO), Ms. Jenifer Sheafer (graduate student at Washington State in radiochemistry), Mr. Zeric Hulvey (graduate student at Notre Dame), and Mr. Patrick Feng (graduate student at UC-San Diego). Workers at Los Alamos received considerable support from the Seaborg Institute for Transactinium Science and NMT-2 to supplement their salaries to be commensurate with comparable LANL students and postdocs.

It is important to note, during the project period, the “Alpha wing” at TA-48 had been closed due to several safety and inventory problems for a total of ~20 months. Dr. Chan was scheduled to begin work at the facility in late 2002 but was only able to spend a total of 8 weeks working at LANL. Dr. Selby began training in the facility in June 2004, but the facility was closed during the lab shutdown in July 2004, and he was not been able to work in the facility for over one year. Subsequently, Dr. Selby was called back to Colorado State to complete work on uranium and thorium chemistry. In 2006, he was able to start work on plutonium chemistry at LANL.

Despite the inaccessibility to the plutonium handling facility at Los Alamos during more than 2 years of the project, we were able to complete a number of studies on Th and U chemistry at Colorado State and several with Dr. Steve Conradson. This work resulted in 18 manuscripts that have been published. A list of those publications may be found at the end of this report. Finally, this work has been presented at 12 international invited symposia, 15 university invited presentations, 4 workshops (NSF and DOE/NSF) and 4 general public talks on actinide chemistry.

II. Project Highlights

Ternary Actinide Structures, AU_2Se_6 ($A = K, Cs$)

A series of ternary chalcogenide ternary compounds have been reported by others, including KTh_2Q_6 ($Q = Se, Te$), $CsTh_2Se_6$, and $CuTh_2Se_6$. These compounds consist of layers of thorium selenide polyhedra that contain an elongated Q-Q bond, which has also been seen in

RbDy_3Se_8 and CsCe_3Te_8 . The formal oxidation state for thorium is most likely tetravalent while the rare earth is most likely trivalent. The oxidation state for the chalcogenide atoms in these phases is difficult to assign but a model of mixed oxidation state selenium has been proposed. Our group has recently synthesized a plutonium analog, $\text{KPu}_3\text{Se}_{8-x}$, which is isostructural to RbDy_3Se_8 but with one partially-occupied selenium site. Plutonium apparently prefers a structure where it behaves more like a rare earth element, while thorium prefers a structure more like a transition metal as found in ZrSe_3 .

We have prepared the uranium analog in this series of compounds, AU_2Se_6 ($A = \text{K}, \text{Cs}$). The compounds are isostructural to the previously reported KTh_2Se_6 . The $[\text{U}_2\text{Se}_6]^-$ layers are similar to the ZrSe_3 and ThSe_3 structure types. For AU_2Se_6 and the thorium analogs, the alkali metal resides within the interlayer spaces of the compound. For $\text{KPu}_3\text{Se}_{8-x}$, the structure is isostructural to RbDy_3Se_8 . The $[\text{Pu}_3\text{Se}_{8-x}]^-$ layer is related to NdTe_2 , NdTe_3 , and PuSe_2 structure types and the alkali metal resides within the interlayer spacing of the $[\text{Pu}_3\text{Se}_{8-x}]^-$ layers. The uranium and thorium structures are related to a transition metal structure, while the plutonium analog is related to a rare earth structure, suggesting a more rare earth like chemistry for plutonium chalcogenides, Figure 1.

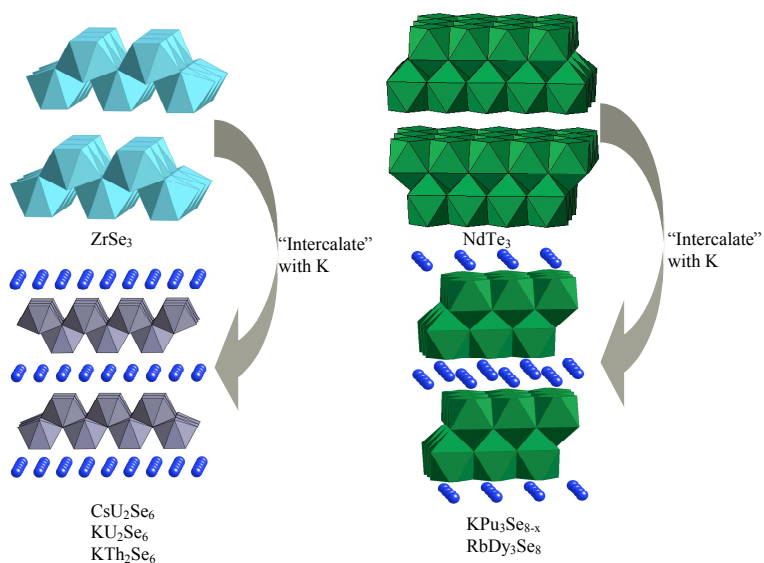


Fig. 1. The relationship between parent structures and alkali actinide selenide compounds is apparent by theoretically “intercalating” the alkali metal between the metal chalcogenide layers.

X-ray Photoelectron spectroscopy (XPS) spectra were collected for KU_2Se_6 to elucidate the oxidation states of uranium and selenium. The binding energy for the $4f_{7/2}$ peak of uranium was at 380.5 eV. The

peak was correlated to the 380.6 eV peak of UO_2 so the formal oxidation state was assigned as +4. Two distinct oxidation states were observed for the $3d_{5/2}$ peak of selenium at 55.3 eV and 53.4 eV. The peak at 53.4 eV was correlated to PbSe , also at 53.4 eV, so the oxidation state can be assigned as -2. The peak at 55.3 eV was correlated to USE , also at 55.3 eV. USE contains a polyselenide network of selenium that makes the oxidation state difficult to assign.

With our Quantum Design MPMS magnetometer at Colorado State University, we were able to obtain magnetic data on the uranium compounds. The $1/\chi$ versus T plots were linear for AU_2Se_6 compounds indicating the materials are paramagnetic. For KU_2Se_6 the magnetic moment was calculated to be 2.79 μ_B , which is consistent for the spin only contribution of U^{4+} with two unpaired electrons.

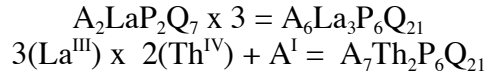
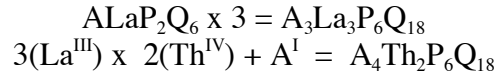
Quaternary Actinide Chalcophosphate Structures, $\text{Cs}_4\text{Th}_2\text{P}_6\text{S}_{18}$ and $\text{Rb}_7\text{Th}_2\text{P}_6\text{Se}_{21}$

The molten alkali metal polychalcogenide flux method has produced a host of novel and complex compounds during this last and the previous project periods. Our group has explored

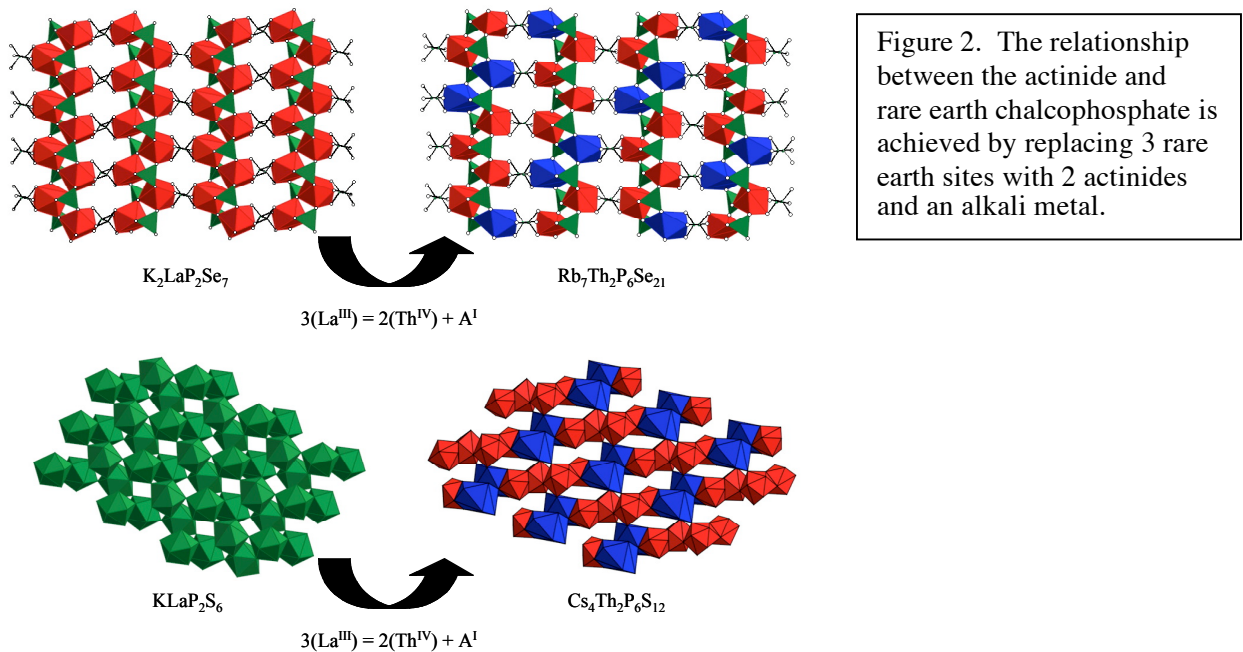
the actinide chalcophosphate phase space and discovered many novel compounds, including α -K₂ThP₃Se₉, Cs₈U₅(P₃S₁₀)₂(PS₄)₄, K₁₀Th₃(P₂S₇)₄(PS₄)₂, A₅An(PS₄)₃ (A = K, Rb, Cs; An = U, Th), K₃Pu(PS₄)₃, and APuP₂S₇ (A = K, Rb, Cs). Our work demonstrated the remarkable diversity of actinide containing chalcophosphate compounds and that the phase space is still ripe to discover more novel compounds.

We have discovered two new thorium chalcophosphates, Cs₄Th₂P₆S₁₈ and Rb₇Th₂P₆Se₂₁, which exist as layered and one-dimensional structures, respectively. Cs₄Th₂P₆S₁₈ crystallizes as colorless blocks in the triclinic space group $P_{\bar{1}}$. The structure consists of (Th₂P₆S₁₈)⁴⁻ layers separated by layers of cesium cations and the layers only contain the (P₂S₆)⁴⁻ building block. Rb₇Th₂P₆Se₂₁ crystallizes as red blocks in the triclinic space group $P_{\bar{1}}$ (no. 2). The structure consists of linear ribbons of (Th₂P₆Se₂₁)⁷⁻ separated by rubidium cations and the ribbon contains both the (PSe₄)³⁻ and (P₂Se₆)⁴⁻ building blocks. Optical band gap measurements correlated the crystal colors and their respective electronic band gaps. Solid state Raman spectroscopy of both compounds confirmed the presence of their respective chalcophosphate building blocks.

Both compounds have no known rare earth analogs; however, the empirical formulae are related to two classes of rare earth compounds, AREP₂Q₆ (A=Na, K; RE=La, Ce, Pr, Sm, Gd; Q = S, Se) and A₂REP₂Q₇ (A = K, Rb, Cs; RE = La, Ce, Sm; Q = S, Se), by the following considerations:



If the actinide is substituted into the rare earth structure, the compound will not charge balance with the rare earth being trivalent and the actinide being tetravalent. An alkali cation is substituted into a rare earth site to form the novel actinide chalcophosphate structures, Figure 2.



Quaternary Actinide Thiocuprate Structures

Besides its key role in high temperature superconductors, copper is an interesting element in a number of chalcogenide-based phases. The lower chalcogenides (S-Te) can stabilize the Cu^+ ion because of lower oxidizing power relative to oxygen. The soft d^{10} ion electronic nature of Cu^+ allows flexible structural and coordination environments including potential Cu^+-Cu^+ interaction (~ 2.7 Å). Cu(I) quaternary compounds offers a remarkable number of new complex structure types; however, no obvious systematic correlation between compounds exist. Fortunately, quaternary systems can be readily mapped and structure/property relationships can be systematically examined. We have worked to complete a study of the K/Cu/An/S (An = Th, U, Pu) quaternary systems.

Thorium containing phases are less well studied than their uranium counterparts. Our early exploration of the K/Th/Cu/S system has yielded three new semiconducting, layered phases, KCuThS_3 , $\text{K}_2\text{Cu}_2\text{ThS}_4$, and $\text{K}_3\text{Cu}_3\text{Th}_2\text{S}_7$ (*Inorg. Chem.*). The compounds vary in their color from colorless (KCuThS_3), red ($\text{K}_2\text{Cu}_2\text{ThS}_4$), and yellow ($\text{K}_3\text{Cu}_3\text{Th}_2\text{S}_7$), which correlate to their respective band gaps of 3.0 eV, 2.0 eV, and 2.4 eV. The band gaps are direct transitions from the narrow Cu/S valence bands to sulfur-based conduction-band states, as seen in the lanthanide and transition metal analogs.

Three new quaternary U^{4+} compounds were synthesized in a similar region of phase-space as the Th compounds described above. KCuUS_3 and $\text{K}_2\text{Cu}_2\text{US}_4$ are isostructural with KCuThS_3 and $\text{K}_2\text{Cu}_2\text{ThS}_4$, Figures 3a, c. The third, $\text{K}_3\text{Cu}_4\text{US}_6$, Figure 3d, features layers of isolated U^{4+} octahedra surrounded by distorted CuS_4 tetrahedra separated by K^+ cations. The charge of $\text{K}_3\text{Cu}_4\text{US}_6$ does not balance as written (assuming Cu^+ and U^{4+}), however, EDS microprobe and single crystal diffraction data support the empirical formula. Oxidation states of the metals were confirmed by XPS to be only Cu^+ and U^{4+} . Charge balance is likely achieved by placing “holes” in the sulfur valence bands, making the material a likely p-type conductor. Crystallography could not distinguish differences between potential S^1/S^{2-} species.

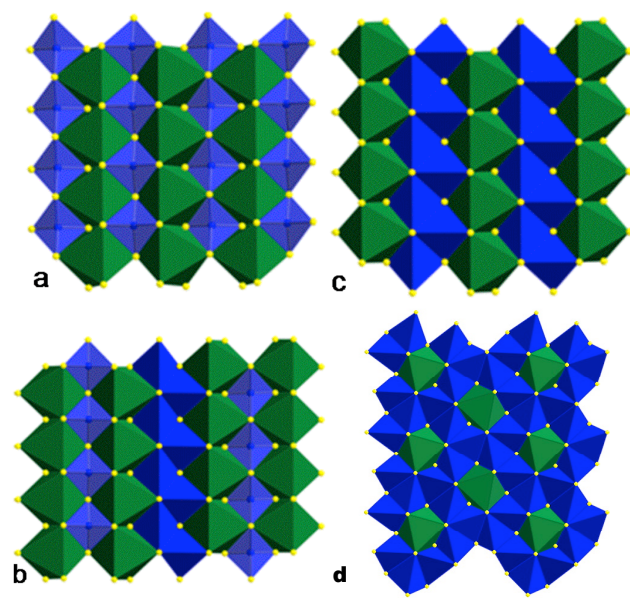


Fig. 3. The actinide chalcocuprates layers are shown, (a) KCuAnS_3 , (b) $\text{K}_3\text{Cu}_3\text{Th}_2\text{S}_7$, (c) $\text{K}_2\text{Cu}_2\text{AnS}_4$, (d) $\text{K}_3\text{Cu}_4\text{US}_6$, where An = U, Th.

As expected, all three uranium-containing compounds display paramagnetic behavior at room temperature and are described in terms of the relative closeness of the U^{4+} octahedra. In $\text{K}_3\text{Cu}_4\text{US}_6$, there would be no expected coupling between uranium cations due to the separation of the uranium octahedra by the CuS_x moieties. In $\text{K}_2\text{Cu}_2\text{US}_4$, there are no interactions between adjacent uranium cations in the linear chains of edge-shared uranium octahedral. KCuUS_3 displays an antiferromagnetic transition at $T_n = 61$ K. In the paramagnetic region above 60 K, the compound exhibits Curie-Weiss behavior with a Weiss constant of -58.4 K indicating a net long range antiferromagnetic behavior. The magnetic moment was calculated to be $2.61 \mu_B$, which is similar to the theoretical spin only contribution.

Metathesis Reactions to Prepare New Materials

We attempted to prepare new and known materials with new Zintl ion salts as metathesis reaction precursors as well as using Cu/CuCl₂ as reactants. We prepared and characterized 5 new ternary “starting material” compounds: K₂P₂Se₆, K₄P₂Se₆, K₃PSe₄, Cs₄Si₂Se₈, and Cs₄Si₄Se₁₀ (see published work, Section III). These phases were reacted with uranium and plutonium chloride salts to demonstrate that reactions with specific tetrahedral phosphate and silicate building blocks could be preformed with actinide halide starting materials rather than the metals (all other previous reactions were run with U and Th metals). We used a halide scavenger (Tl) to try to help the reactions proceed to completion. However, in the case of Pu, a new Pu-doped thallium salt was isolated and characterized: Pu-TlCuS₂, Fig. 4. While this is a known structure type, this demonstrated for the first time the ability to utilize preformed salts as reactants to with PuCl₃.

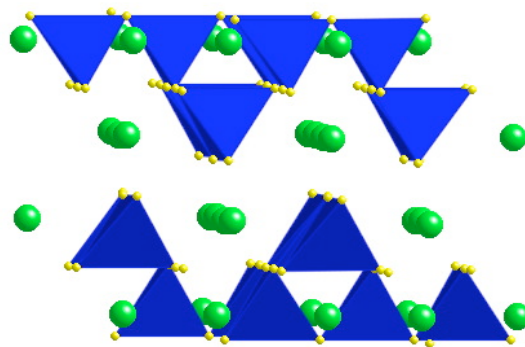


Fig. 4. Pu-TlCuS₂, with green Pu/Tl spheres and blue Cu tetrahedra.

Alkali Metal Precursor Materials.

During the exploration of quaternary phase space, novel ternary structures are often discovered. In an attempt to make a selenium analog of K₅Th(PS₄)₃, a novel ternary structure, K₂P₂Se₆ crystallized along with KTh₂Se₆. K₂P₂Se₆ consists of linear chains of ethane-like P₂Se₆ building blocks that are connected by a Se-Se bond, Figure 5a. Raman spectroscopy showed the presence of the P₂Se₆ building block along with a stretch consistent with a Se-Se bond. This material is particularly interesting because it represents the high pressure phase of KTbP₂Se₆. The rare earth material was placed under high pressures, ~9.2 Gpa, in a diamond anvil cell and underwent a phase transition accompanied by a shift in absorption edge to red and a formation of a Se-Se bond. The same absorption edge and linear chain selenophosphate structural motif are seen in both K₂P₂Se₆ and high pressure KTbP₂Se₆.

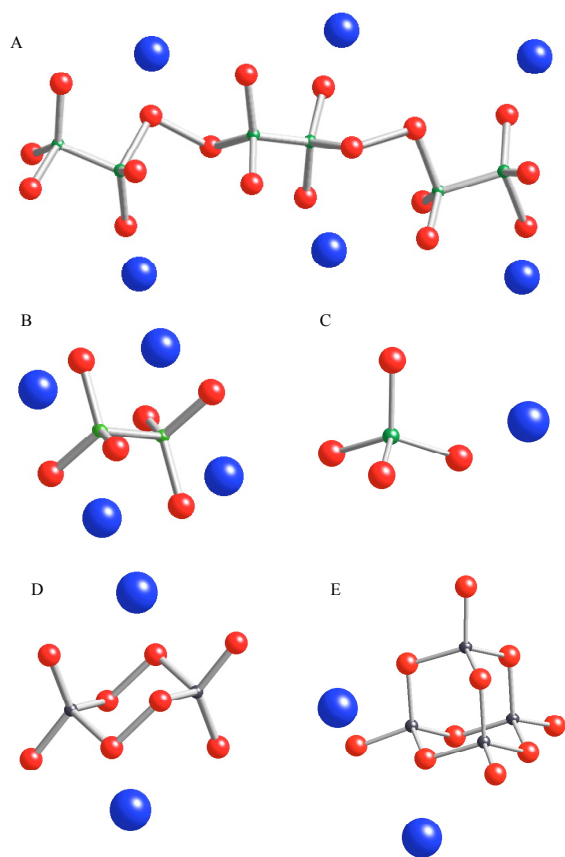


Figure 5. New ternary “starting material” compounds, (a) K₂P₂Se₆, (b) K₄P₂Se₆, (c) K₃PSe₄, (d) Cs₄Si₂Se₈, and (e) Cs₄Si₄Se₁₀. Blue spheres are the alkali metal, red spheres are selenium, green spheres are phosphorous, and gray spheres are silicon.

The ternary (K-P-Se) phase diagram was explored and $\text{K}_2\text{P}_2\text{Se}_6$ was prepared without thorium. Two unpublished potassium selenophosphates, K_3PSe_4 and $\text{K}_4\text{P}_2\text{Se}_6$, were discovered. K_3PSe_4 consists of $(\text{PSe}_4)^{3-}$ tetrahedra surrounded by K cations, Figure 5c. The compound is isostructural to K_3PS_4 . $\text{K}_4\text{P}_2\text{Se}_6$ consists of ethane-like $(\text{P}_2\text{Se}_6)^{4-}$ units surrounded by K cations, Figure 5b. The compound is isotypic to $\text{Tl}_4\text{P}_2\text{Se}_6$. The phase diagram indicated that K_3PSe_4 forms at the selenium rich region of phase space, where the conditions are highly oxidizing. $\text{K}_2\text{P}_2\text{Se}_6$ and $\text{K}_4\text{P}_2\text{Se}_6$ formed in reactions containing less selenium indicating less oxidizing conditions are required so that P^{4+} and Se^- are incorporated into the compound. $\text{K}_4\text{P}_2\text{Se}_6$ forms the region of phase space that is higher in potassium concentration as compared to $\text{K}_2\text{P}_2\text{Se}_6$.

We have attempted to make a uranium analog to the rare earth chalcosilicate, KLaSiSe_4 . A new ternary, $\text{Cs}_4\text{Si}_2\text{Se}_8$, was serendipitously discovered. The structure consists two tetrahedra of SiSe_4 bound by an Se-Se bond to form a ring complex of $(\text{Si}_2\text{Se}_8)^{4-}$ surrounded by Cs cations, Figure 5d. The compound is isostructural to $\text{Cs}_4\text{Ge}_2\text{Se}_8$. While attempting to make $\text{Cs}_4\text{Si}_2\text{Se}_8$ without the presence of uranium, we also discovered $\text{Cs}_4\text{Si}_4\text{Se}_{10}$, which crystallizes with adamantane-like $[\text{Si}_4\text{Se}_{10}]^{4-}$ units composed of four corner shared SiSe_4 units and Cs cations charge balancing the compound, Figure 5e. The compound is isostructural with $\text{Cs}_4\text{Ge}_4\text{S}_{10}$. These new ternary compounds will be used as “starting materials” for a series of metathesis reactions that we hope will result in several new target phases that may be explored by other groups in future years.

III. Manuscripts Resulting from ER 15351

- P. M. Briggs-Piccoli, K. D. Abney, J. R. Schoonover, P. K. Dorhout "Synthesis and Structural Characterization of Quaternary Thorium Selenophosphates: $\text{A}_2\text{ThP}_3\text{Se}_9$ (A = K, Rb) and $\text{Cs}_4\text{Th}_2\text{P}_5\text{Se}_{17}$ " *Inorg. Chem.*, **2000**, 39, 2970-2976.
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- B. C. Chan, P. L. Feng, P. K. Dorhout "Crystal Structures of Potassium Terbium(III) Tetrasulfidogermanate, KTbGeSe_4 and Potassium Praseodymium(III) Tetraselenogermanate, KPrGeSe_4 and" *Z. Krist.* **2005**, *220*, 7-8.
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- A. K. Gray, J. M. Knaust, B. C. Chan, L. A. Polyakova, and P. K. Dorhout "Crystal structure of potassium ytterbium(III) tetrathiosilicate(IV), KYbSiS_4 " *Z. Krist.* **2005**, *220*, 293.
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distribution and local structure and speciation in the UO_{2+x} and PuO_{2+x} binary oxides for $x \geq 0.25$ ” *J. Solid State Chem.* **2005**, 178, 521-535.

H. D. Selby, B. C. Chan, J. D. Thompson, E. P. Luther, K. D. Abney, P. K. Dorhout “Synthesis and Characterization of a New Family of U-Based Quaternary Phases in the K/Cu/U/S System,” in preparation for *Inorg. Chem.*